

Current Chemical Hazard Characterization Practices in DOE Complex and Suggested Recommendations

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PS-4

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LA-UR-03-7857

Background

- There is no single DOE Standard for non-nuclear (chemical) safety, similar to nuclear safety (DOE-STD-3009).
- 10 CFR 830 Rule mentions to analyze for chemical hazards but provides no guidance for SC, HC, HA, and AA.
- 10 CFR 830 Rule does not apply to pure non-nuclear facilities.
- No evaluation guide (EG) for chemical hazards for Worker and Public.
- Various DOE sites including LANL have developed their Chemical Safety program without consistent guidelines.

CSTC Project 2003-C “Current Chemical Hazard Characterization Practices” *J. C. Laul, LANL, Chair*

Objectives

- Provide a best practice model for a high quality Chemical Safety Analysis (CSA) program; and
- Mitigate wide variations and improve process quality, to reduce potential risk for the workers and the public throughout the DOE complex.

Phase I: Gather information from the existing non-nuclear related documents from DOE sites and summarize them for similarities and differences; analyze for missing or undeveloped information.

Phase II: Develop best practices/recommendations for Chemical Hazard Categorization (CHC) and CSA program.

Adoption of Phase II is voluntary.

Report Format

CHEMICAL SAFETY ANALYSIS PRACTICES

SITE NAME

LOS ALAMOS NATIONAL LABORATORY

Introduction (a few lines of description on the mission of your site)

1.0 Chemical Hazard Category

1.1 Screening Criteria

1.2 Frequency Binning

1.3 Receptors

1.4 Chemical Consequence

1.5 Risk Binning

1.6 Functional Classification (Safety Control Selection)

2.0 Hazard Baseline Methodology

2.1 Hazard Checklist Criteria

2.2 Hazard Identification

2.3 Additional Hazard Evaluation

2.4 Common Hazard Screening Criteria

2.5 Example of Hazard Evaluation Table

2.6 Consequence/Source Term Determination Method

3.0 Safety Document

3.1 Format and Contents of Safety Documents

3.2 USQ-Like Process for Non-Nuclear Facilities

DOE Sites Covered

#	DOE Site	POC/Author (Thanks for Contribution)
	DOE-HQ/EH, DOE-HQ/NNSA	Dan Marsick, Rob Vrooman
1	SRS	Michele Baker, J.C. Laul
2	Pantex+	Shawn Spivey, Ron Frymoyer
3	INEEL	Larry Lee
	Hanford, RL	Joe Eizaguirre (DOE-RL)
4	Hanford, ERC	Jannifer Ollero, Mike Maxon
5	Hanford, Fluor	Craig Clairmont
6	Hanford, PNNL	Tonia Graham
7	Hanford, CHG (CH2MHILL)	Brad Evans
8	LANL	J. C. Laul
9	LLNL+	Charlotte Van Warmerdam, J. C. Laul
10	SNL	Sylvia J. Saltzstein, Stephen A. Coffing
11	ORNL, UT/Battelle	Ann Shirley Murphy, David Renfro
12	Oak Ridge, Bechtel Jacob	Charlie Satterwhite
13	Y-12 Plant	Jim Goss, H.F. Hartman
14	RFETS*	Mitchell Waller , Marco S. Colalancia,
15	ANL-E	J. Woodring, G. Winner, G. Pierce
	WV, Mound, Fernald	Lydia Boada-Clista (DOE-OH)
16	West Valley	Kelly Albamonti, Michele Baker
17	Mound (MCP)*	W.R. Henderson, Danny Punch, Larry Lee
18	Fernald (FEMP)*	Rich Lowery, Pat Fisk
19	BNL	Steve Hoey

*D&D and closure; + Sites are revising their chemical safety procedures.

Section 1. Facility Chemical Hazard Category and Screening Criteria

There are wide variations in hazard category (HC) terminology and in the screening criteria used to define the HC in terms of:

- High/Moderate/ Low HC
- Some HC are based on inventory criteria
- Some HC are based on consequence criteria
- Significant variations in inventory criteria
 - 40 CFR 68, TQ
 - 29 CFR 1910, TQ (PSM)
 - 40 CFR 355, TPQ
 - 40 CFR 302, RQ
- Significant variations in consequence criteria
 - ERPG-3, offsite vs. onsite
 - ERPG-2, offsite vs. onsite
- Hybrid combination (inventory & consequence)

Phase II. Recommendations for Non-Nuclear CSA Program in the DOE Complex Team Members

#	DOE Site	Name
1	LANL	J.C. Laul, Chair
2	DOE-HQ/EH	Dan Marsick
3	DOE-HQ/NNSA	Rob Vrooman
4	SRS	Kevin O,Kula
5	INEEL	Larry Lee
6	Pantex	Shawn Spivey
7	PNNL	Tonia Graham
8	LLNL	Charlotte Van Warmerdam
9	Fernald, DOE-OH	Lydia Boada-Clista

Phase II. Sections 1.0 Facility Chemical Hazard Class

Category	Inventory Based Thresholds	Consequence Based Thresholds*
High (H)	>29 CFR 1910.119, TQ	>ERPG-3 @ SB (Offsite)
Moderate (M)	<1910 TQ - >40 CFR 355, TPQ	>ERPG-3 @ onsite (100m)
Low (L)	<355, TPQ - > 40 CFR 302, RQ	>ERPG-3 @ ~10m (local worker)+
Industrial (I)	<40 CFR 302, RQ	---

* If ERPG-3 values are not available, TEEL-3 values should be used.

>1910 TQ requires safety analysis; Consequence may not be reliable for <100m.

+ TBD by local site.

Sections 1.1 Hazard Class Screening Criteria

Inventory: TQ, 29 CFR 1910.119 (Threshold Quantity)
TPQ, 40 CFR 355 (Threshold Planning Quantity)
RQ, 40 CFR 302 (Reportable Quantity)

Consequence: ERPG-3 or TEEL- 3

Section 1.2 Frequency Evaluation (Binning)

DOE Site	Frequency Criteria	Comment
SRS, INEEL, Y-12 Plant, RFETS, Hanford Fluor, Oak Ridge-Bechtel Jacob, WV, Mound, Fernald	<ul style="list-style-type: none"> STD-3009 (4 levels) 	AN $10^{-1} > f < 10^{-2}$ UN $10^{-2} > f < 10^{-4}$ EN $10^{-4} > f < 10^{-6}$ BEU $10^{-6} > f$ Not credible
Pantex (4 levels)	<ul style="list-style-type: none"> Frequent to likely, L4 STD-3009 	L4 to L1 level: L3 (UN); L2 (EU); L1 (BEU)
LANL (5 levels)	I, ($>10^0/\text{yr}$) II, ($<10^0/\text{yr}$ to $>10^{-2}/\text{yr}$) III, ($<10^{-2}/\text{yr}$ to $>10^{-4}/\text{yr}$) IV, ($<10^{-4}/\text{yr}$ to $>10^{-6}/\text{yr}$) V, ($<10^{-6}/\text{yr}$)	Frequent (expected) Probable (Likely) Occasional (Unlikely) Improbable (EU) Remote (BEU)
LLNL (No frequency cited, 5 levels)	<ul style="list-style-type: none"> Very Likely Likely UN EU Less than Credible 	Often Several times in life of facility Once during life cycle of facility DBA BDB
BNL (No frequency cited, 6 levels)	<ul style="list-style-type: none"> A, Frequent B, Probable C, Occasional D, Remote E, Extremely remote F, Impossible 	Occur repeatedly Several times in life cycle Sometimes in life cycle Not likely to occur in life cycle Probability is nearly zero Impossible

Phase II. Sections 1.2 Frequency Evaluation (Ranking)

Five levels of frequency are recommended. **Four levels** are from DOE-STD-3009 and an additional as normal or frequent with a frequency once per year to 10 years is added, shown below:

- Normal (NR) 10^0 to 10^{-1}
- Anticipated (AN) 10^{-2} to 10^{-1}
- Unlikely (UN) 10^{-4} to 10^{-2}
- Extremely Unlikely (EU) 10^{-6} to 10^{-4}
- Beyond EU (BEU) Less than 10^{-6}

Normal facility operation includes routine events with a frequency once per year to 10 years. This frequency can be combined with the AN to give a 10^{-2} to $10^{-0}/y$ frequency.

UN, EU, and BEU are same from STD-3009.

Section 1.3 Receptors (Dose Receivers)

DOE Site	Onsite-1 Worker	Onsite-2 Worker	Public/ Offsite	Comment
SRS, ANL-E, Oak Ridge-BJ	Imm.	Outside	X	Onsite-1; Inside facility Onsite-2; Outside facility
Pantex, LANL, LLNL, WV	X		X	Imm. or co-located
INEEL, RFETS	Imm.	100m	X	
Hanford, ERC	X		X	
Hanford, Fluor BNL	X	X	X onsite X offsite	Onsite-2; co-located at 100m
PNNL	X or 100m		X	
SNL	X		X	Inside facility
Y-12 Plant	Involved worker and at 100m		X	
Mound (MCP)	Imm.	50m	X	Onsite-2 at 50m
Fernald (FEMP)	X		X	Imm/co-located at 30m

Phase II. Sections 1.3 Receptors (Dose Receivers)

Receptors are recommended at 3 distances:

- **Public - Site Boundary (Offsite)**
- **Worker (onsite-2) – Onsite at 100m (co-located)**
- **Worker (onsite-1) – at ~10-30m (immediate or facility, TBD by site)**

Section 1.4 Chemical Consequence Evaluation

- There are some important variations in the CC criteria used for onsite-1 and onsite-2 workers and the public by the various sites.
- DOE standardized EGs should be helpful in mitigating these variations.
- **Consequence Class:** High/ Moderate/ Low/ Negligible
A/B/C/D/E
No Category - Death to minor injury, based on HA
Prompt death to less than serious injury

Criteria: IDLH
ERPG-3; ERPG-2; ERPG-1
PEL-TWA, TLV-TWA

DOE-STD-3009-94 (ERPG-3 or -2)

High - Considerable onsite and offsite impacts on people or the environment
Moderate - Considerable onsite impact on people/environment; minor offsite
Low - Minor onsite and negligible offsite impact on people/environment
No - Negligible onsite and offsite impact on people/environment

Phase II. Sections 1.4 Chemical Consequence Evaluation

Category	Consequence*
High (H)	>ERPG-3 or Immediate health effects or loss of life
Moderate (M)	>ERPG-2 or Severe injury, illness, disability
Low (L)	>ERPG-1 or Minor injury, illness, no disability
Negligible (N)+	<ERPG-1 or No harm or no measurable consequence
* Consequence may not be reliable for <100m. + Controlled by ISM or ISP	

•Applies to both workers and public.

Section 1.5 Risk Binning Matrix

DOE-STD-3009-94: 3 x 3 Matrix = Risk 1 → 9 ; 9>8>7>...2>1

DOE Site	F x C	Onsite/Public	Comment
SRS, Y-12 Plant	4 x 4	1 → 11; 1>2>3...11	
Pantex	4 x 4	Safety items as controls are required in high risk events.	No risk ranking is provided.
INEEL, LLNL	4 x 4	1 → 16 ; 16>15>...>1	1>2>3.....>16 for LLNL, Reverse
LANL	5 x 5	1 → 4; 1>2>3>4	For Risk 1, work will not be performed.
Oak Ridge, BJ	4 x 4	A → D ; A>B>C>D	
RFETS	3 x 3	I → IV; I>II>III>IV	
West Valley Mound	3 x 3	STD-3009; 1 → 9; 9>8>...1	
Fernald	4 x 4	Significant	No Risk #

Phase II. Sections 1.6 Risk Binning Matrix (5x4)

Risk-binning matrix (1-4) applies to both **worker** and **public**.

Frequency/Consequence	Negligible (N)	Low (L)	Mod. (M)	High (H)
Normal (NR)	ISM/ISP Program 4	3	2	1
Anticipated (AN)	4	3	2	1
Unlikely (UN)	4	4	3	2
Extremely Unlikely (EU)	4	4	4	3
Beyond Extremely Unlikely (BEU)	4	4	4	4

Controls Recommended:

Passive Design or OSRs or High Safety Features (Risk 1): H-NR, H-AN

Passive Design or OSRs or Moderate Safety Features (Risk 2): H-UN, M-NR, M-AN

Design Standards or DiD, AC; (Risk 3): H-EU, M-UN, L-AN, L-NR

ISM/ISP Programs (Risk 4):

Risk ranking of 1 is not acceptable and requires additional controls to reduce the risk.

Risk rankings of 2 and 3 require management approval.

Section 1.6 Safety Control Selection:

Some Preliminary Trends Identified

- There are no chemical consequence EGs provided by DOE and none used by DOE site contractors to give a Safety Class Classification.
- Some sites have developed their own EGs based on **consequence** or **risk**.
- However, there is **no correlation** between the **Inventory or Consequence** based Facility HCC to **Consequence or Risk** criteria for EG for SS, DiD, and AC.
- Different EG criteria are used for SS, DiD and AC:
 - PEL-TWA, ERPG-1, -2, -3
 - TLV-TWA, ERPG-1, -2, -3
 - ERPG-1, -2, -3
 - ERPG-2
 - ERPG-2, IDLH
 - ERPG-2, ERPG-3

There is no consistency in the selection of ERPGs or TEELs for EG for SS, DiD, and AC.

Phase II. Sections 1.2 Safety Control Selection

The safety control selection can be based on **consequence** or **risk** criteria.

- **EG for control selection is recommended as ERPG -3/TEEL -3.**
- Safety controls can be high safety features and moderate safety features.
- OSRs are administrative control for high and moderate consequences.
- Other administrative controls include specific administrative control (AC), institutional safety program (ISP), and integrated safety management (ISM).

Category	Controls Criteria	Control Thresholds	Safety Controls, SSCs
High	Consequence or risk	ERPG-3	OSR, High Safety Features
Moderate	Consequence or risk	ERPG-3	OSR, Moderate Safety Features
Low	Consequence or risk	ERPG-3	AC, ISM or ISP
Industrial	Consequence or risk	---	ES&H/ISM

Section 2. Hazard Baseline Methodology (HBM)

- Most sites have some form of HBM in place. However, the details vary depending on the complexity of their CSA program. Some sites use the ISM five core steps as part of Chemical Safety practices. Discussions on hazard checklist category and hazard identification do not appear to correlate with the facility HC level of High/Moderate/Low.
- The sites hazard evaluation tables list key features such as event description, hazards, root cause, unmitigated and mitigated frequency, consequence, and risk, and controls (EC, AC), although format varies from site to site. In some cases, comparisons of unmitigated and mitigated features are not provided in the evaluation tables.
- Chemical dispersion models X/Q method, ALOHA, and EPICode are commonly used for dose calculations and appear reliable, although other models are also used for specific purpose.

Phase II. Section. 2.0 HAZARD BASELINE METHODOLOGY

Hazard baseline methodology (HBM) is usually qualitative and involves:

- Hazards Checklist
- Hazard Identification
- Additional Hazard Evaluation (chemical mixing & incompatibility)
- Common Hazards Screening Criteria
- Hazard Analysis (HA)
- Example of a Hazard Evaluation Table
- Accident Analysis (AA), Dispersion Model

Most of the information is presented in a tabular form. Hazard analysis can be qualitative or quantitative depending on the facility chemical hazard classification.

Most of the sites have some form of HBM in place, however, the details vary depending on the complexity of their chemical safety program.

Phase II. Section 2.1 Hazard Checklist Category

Section 2.2 Hazard Identification (HI)

Hazard checklist category and HI followed by the various DOE sites are satisfactory.

Five core steps of ISMS, followed by some sites, are recommended.

- Define work
- Identify and analyze hazards
- Develop and implement controls
- Perform work safely
- Ensure performance & continuous improvement.

Phase II. Sections 2.3 Additional Hazard Evaluation (AHE)

Most sites use AHE as mixing of chemicals or incompatible chemicals that can cause violent reaction (e.g, explosion). Process knowledge should be used in mixing chemicals and assessing hazards.

Non-chemical hazards (mechanical equipment) that can trigger chemical hazards should also be considered.

Phase II. Sections 2.4 Common Hazard Screening Criteria

Hazardous chemical: Toxic, Corrosive, Reactive, Ignitable, Incompatible

Screening Criteria: RQ 40 CFR 302

TPQ 40 CFR 355)

TQ 29 CFR 1910.119

- **The chemicals that do not screen out are further considered for evaluation for hazard and accident analysis (qualitatively or quantitatively) and selection of controls.** All hazards below the screening criteria should be evaluated by the techniques in ISM.
- Chemicals not appearing on the RQ list should be checked for the hazard characteristics in the TPQ and TQ.
- There are other OSHA type common hazards such as pressure, temperature, and voltage, which can be screen out, however, they can serve as initiators for accidents involving hazards. Flammable materials, leak of materials, and equipment failure are other examples of common hazards, which can serve as initiators for accidents.

Phase II. Sections 2.5 Hazard Analysis (HA) and an Example

Preliminary Hazard Analysis (PHA) should consist of safety analysis team member with different expertise and should involve inspection of the facility, chemical processes, identification of hazards, and controls.

HA should be performed using techniques such as:

- What-If/Checklist Analysis
- Hazard and Operability Analysis (HAZOP)
- Failure Modes and Effects Analysis (FMEA)
- Fault Tree Analysis (FTA)
- Event Tree Analysis (ETA)

An example of an H&CET that can include accident analysis (qualitative and quantitative) should capture the following features:

- Hazards
- Event category and description
- Root cause
- Frequency Ranking - Unmitigated and Mitigated (Preventor and Mitigator)
- Consequence Ranking - Unmitigated and Mitigated
- Risk Ranking - Unmitigated and Mitigated
- Controls (e.g., EC, AC)

Table A: An Example of Completed Hazard Evaluation Table

No.	Event Category & Hazard	Event Description	Causes	Unmitigated			<u>Controls</u> Preventive (P) Mitigative (M)	Mitigated		
				Freq. Level	Conseq. Level	Risk Rank		Freq. Level	Conseq. Level	Risk Rank
#1	Explosion Ex-1 Chemical reaction	Ammonium nitrate is mixed with organic matter & forms explosive mixture by heat. Onsite worker injury	Human error Lack of work instructions	NR	Onsite-1: High Onsite-2: Mod. Offsite: Neg	1 2 4	<ul style="list-style-type: none"> •No heat source, P •Hood or shield, M •PPE, M •Trained personnel, P, M •Work instructions, M 	UN	Onsite-1: Mod. Onsite-2: Low Offsite: Neg.	3 4 4

Phase II Sections 2.6 Consequence/Source Term Determination Method

For quantitative results of HA, chemical dispersion models commonly used:

- **X/Q method (MACCS2, RSAC-6)**
- **ALOHA**
- **EPICode**

Although other models such as HG SYSTEM, SCREEN3, ARCON96, and ARCHI are also used for specific purpose.

Many sites use F stability class, 1 m/s wind speed, and 1 cm/s deposition velocity for initial consequence calculations as being conservative with weather conditions. These codes use a Gaussian dispersion plume. Equation used is as follows.

$$\text{Concentration (mg/m}^3\text{)} = [Q / Q \times \text{MAR} \times \text{ARF} \times \text{RF} \times \text{DR} \times \text{LPF}]1/T \dots\dots\dots(1)$$

ARF and RF can be taken from DOE-HDBK-3010-94 and DOE-STD-1027-92.

Release time and sampling time are typically 10 or 15 minutes.

ALOHA and EPICode are well developed computer codes that require input such as weather conditions (stability class A-F), temperature, wind speed, release height, and distance from release. These models use Gaussian dispersion plume and yield concentration (mg/m³ or ppm) at a given distance (onsite-1 & onsite-2 workers, and public). These values are then compared with the ERPG-1, -2, -3 or TEEL-1, -2, -3.

Section 3.Safety Document: Format, Content, & USQ-Like Process and DOE/NNSA Approval for Non-nuclear Hazard Category (HC)

- Some sites use graded approach (DSA/ASA or SAR/HAR) for High/Moderate/Low HC
- Some sites use only ASA for both High/Low HC
- Some sites use FUA, 4 elements of PSM for HC
- Some DSA/ASA or SAR/HAR have no standard format but contents are well defined
- Some DSA/ASA or SAR/HAR have defined format and content

DOE/NNSA Approval

- Some sites do not require DOE/NNSA approval for H/M/L HC documents
- Some sites require DOE/NNSA approval for all H/M/L HC documents
- Some sites require DOE/NNSA approval for H/M and not for Low HC documents
- **USQ-Like process follows the same protocol for approval for H/M/L**

Phase II. Sections 3.0 Safety Document

Section 3.1 Format and Content of Safety Document

Section 3.2 USQ-Like Process

- a. **HC:** Recommendations for H/M/L HC are listed in Sections 1.0 & 1.1.
- b. **Safety Analysis Document (SAD):** SAD can be with a graded approach or ASA depending on the complexity of the CSA program.
- c. No requirements for format, but the contents should be well defined to include the needed information for the SAD/ASA or SAR/HAR.
- d. **DOE/NNSA Approval:**
- e. **1) DOE/NNSA Site Office approval is required for High HC.**
 - 2) *The Moderate hazard facility would be approved by the Contractor and sent to DOE/NNSA for concurrence.*
 - 3) The Low HC would be approved only by the Contractor. There would be no DOE/NNSA involvement unless specified by DOE/NNSA.
- e. **USQ-Like Process:**
 - a. **DOE/NNSA Site Office approval is required for High HC.**
 - b. *The Moderate hazard facility would be approved by the Contractor and sent to DOE/NNSA for concurrence.*
 - c. The Low HC would be approved only by the Contractor. There would be no DOE/NNSA involvement unless specified by DOE/NNSA.

Summary: Chemical Safety Analysis (CSA) Program

Phase 1:

There are wide variations in approaches to Chemical Safety Practices among the various DOE Sites as described in subsections of Sections 1,2, and 3, in terms of:

- Section 1. HC and screening criteria; Frequency; Receptor selection; Chemical consequence evaluation criteria; EG, Risk binning matrix; and Safety control selection.
- Section 2. Hazard Baseline Methodology and its various aspects.
- Section 3. Safety document requirements in terms of: Format and content; USQ-like process; and approval by DOE/NNSA.
- Some variation in HC, HBM, and safety document requirements are understandable and normal depending on the level of complexity of the CSA program across the DOE site.

Phase II. Provides best practices/recommendations and some flexibility in the CSA program including HC & SC, consequence, risk binning, EGs, and selection for safety controls in order to mitigate wide variations, improve process quality, and reduce potential risk for the onsite workers and the public.

- Adoption of Phase II is voluntary.